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POLAR GASES AND THEIR EQUIMOLAR MIXTURES

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ABSTRACT

Thermal-conductivity measurements have been carried out over the temperature range 300° to 475° K with an eight-cell hot-wire thermal-conductivity apparatus. The thermal conductivities of the deuterated gases are greater than those of their unsubstituted counterparts at the higher temperatures (presumably because of their higher heat capacities). Conductivities of the equimolar mixtures lie about midway between the conductivities of the pure components. Results are analyzed to test a recent hypothesis that a resonant exchange of rotational quanta causes the thermal conductivity of a polar gas to seem anomalously low in relation to its viscosity. These results are consistent with this hypothesis, the only qualification being that near-resonant exchange is also important.

INTRODUCTION

The thermal conductivities of highly polar gases such as hydrogen fluoride, water, and ammonia appear to be anomalously low in relation to their viscosities. Mason and Monchick¹ have suggested that this effect is largely a result of a resonant exchange of rotational energy, presumed probable on grazing self-collisions of polar molecules. Hence, a grazing collision with exchange is equivalent to a head-on collision without exchange insofar as the transport of the rotational quantum is concerned. Baker and Brokaw² have recently measured the thermal conductivities of gaseous H_2O and D_2O , as well as their equimolar mixture,

in an effort to test experimentally the theory of Mason and Monchick. As has been previously pointed out,² a polar gas and its deuterated counterpart should be a good test of the theory because the substitution of a deuterium atom for a hydrogen atom increases the moment of inertia by approximately a factor of two but changes the mass only slightly. Since the resonant correction depends inversely on the $3/2$ power of the moment of inertia, the resonant correction for the deuterated gas will be approximately one third that of the ordinary gas.

The following conclusions were reached on the basis of the work with the $\text{H}_2\text{O}-\text{D}_2\text{O}$ system:²

(1) The data of the pure compounds seem to confirm Mason and Monchick's postulate regarding the importance of resonant transfer or rotational quanta.

(2) On the other hand, the data on the mixtures suggest that a resonant exchange of rotational quanta is not an important factor in determining the thermal conductivity of water vapor.

(3) It was suggested, tentatively, that exchange of rotational energy or grazing collisions is important but is of a classical nature.

These conclusions were not definitive because of inadequacies both in the theory for asymmetric top molecules (such as water) and in the theory for polyatomic gas mixtures. In addition, it has been pointed out^{3,4} that the $\text{H}_2\text{O}-\text{D}_2\text{O}$ system was in fact an equilibrium ternary mixture of H_2O , HDO , and D_2O . One way to overcome the first shortcoming is to study gas pairs for which the theory does exist; namely, linear dipoles such HCl and DCl , and symmetric tops, such as NH_3 and ND_3 . As for the second point, the work by Mason and Monchick on the thermal conductivity of polyatomic and polar gases¹ has recently been extended to include gas mixtures.⁵

The thermal-conductivity equations obtained by Mason and Monchick are based

on the formal kinetic theory of Wang-Chang and Uhlenbeck⁶ and Taxman.⁷ However, Waldman⁸ has recently pointed out that certain simplifying assumptions made in both these theories are not valid; therefore, neither of these theories is actually as rigorous as it had previously been considered to be. Consequently, the equations of Mason and Monchick must also be regarded as less rigorous. Nonetheless, their formulas for calculating the thermal conductivity of polyatomic and polar gases appear to be the best presently available and will be used in the data analysis of this work.

The experiments reported in this paper were undertaken to determine whether the tentative conclusions reached with $\text{H}_2\text{O}-\text{D}_2\text{O}$ are correct. Conductivities of NH_3 , ND_3 , HCl , DCl , CH_4 , CD_4 and equimolar mixtures of $\text{HCl}-\text{DCl}$ and CH_4-CD_4 were measured in the temperature range 300° to 475° K. The conductivities of N^{15}H_3 and the equimolar mixture of N^{15}H_3 and NH_3 were measured at 300.0° and 424.4° K, while the conductivity of the equimolar NH_3-ND_3 mixture was measured at 300.0° K only.

EXPERIMENTAL

Apparatus and Procedure

The hot-wire thermal-conductivity apparatus used for these conductivity measurements consists of four pairs of carefully matched platinum-iridium filaments mounted in a stainless-steel block. The cells are connected as elements of a constant current Wheatstone bridge. When an instrument such as this is used as a thermal-conductivity detector in analytical work, as is often the case, a bridge current of 400 to 500 milliamperes is normally used. Under these conditions, the difference between the temperature of the hot wires and the temperature of the block, ΔT , is 300° to 400° C. For this work, however, a bridge current of only 100 milliamperes was used, which produces a ΔT ranging from 2° to 25° C, depend-

ing on the thermal conductivity of the gas in the cells.

The voltage unbalance produced when gases of unequal thermal conductivity were introduced into the test and reference cells was measured on a sensitive potentiometer. The instrument responds to the reciprocal of the thermal conductivity,

$$E - E_{\text{ref}} = b \left(\frac{1}{\lambda} - \frac{1}{\lambda_{\text{ref}}} \right), \quad (1)$$

where E is the voltage unbalance with a gas of unknown conductivity in the four test cells and a reference gas in the other four cells; E_{ref} is the voltage with the reference gas in all eight cells; λ and λ_{ref} are the thermal conductivities of the unknown and reference gases, respectively; and b is a constant characteristic of the apparatus (it may be slightly temperature dependent). For this work, nitrogen was used as the reference gas, and helium and argon were used as the calibrating gases.

All the thermal-conductivity measurements were made at atmospheric pressure (750 torr). The desired temperatures were maintained by a large oil bath that could be controlled to within $\pm 0.02^\circ \text{C}$. Temperature measurements were made with a platinum resistance thermometer. The gas handling system was conventional in all respects. Since all the gases used in these experiments are readily condensed by liquid nitrogen, transfer of a gas from a storage vessel to the test cells and back to the storage vessel was readily achieved by strategically placed cold fingers.

As previously mentioned, nitrogen was generally used as the reference gas; however, all the isotopically substituted gases as well as the equimolar mixtures were measured against their nonsubstituted counterparts, that is, ND_3 against NH_3 , DCl against HCl , etc. Thus, these small electromotive forces were measured with

enhanced precision.

Voltages relative to argon are recorded in Table I. The measurements for each system were not made at identical temperatures, since measurements for a given system were made over the entire temperature range before changing to another gas pair. The experimental voltages were reproducible to better than ± 0.005 millivolt. Because helium and argon are monatomic gases, it is possible to compute conductivity from viscosity through a rigorous, experimentally verified, theoretical relation, to less than a few parts per thousand. Thus, thermal conductivities for the calibrating gases were assigned after considering both experimental viscosity and thermal-conductivity data. The details of this method have been fully described previously.² The conductivities selected for calibration are given in Table II.

Experimental Results

The thermal conductivities derived from Tables I and II by means of Eq. (1) are presented in Table III. The table is again subdivided into three parts since the measurements for the different systems were not made at identical temperatures. Although the primary purpose of this work is to measure accurately the relative differences between the ordinary gases used and their isotopically substituted counterparts, the absolute values obtained are generally in agreement with the literature. This is illustrated in Fig. 1, where the present data on ammonia are compared with the recent measurements of Richter and Sage.⁹ The agreement seems satisfactory.

ANALYSIS AND DISCUSSION

The expression that Mason and Monchick¹ derived for the thermal conductivity of a polyatomic gas may be written as follows:

$$\lambda = \frac{\eta}{M} \left[\frac{5}{2} C_{v_{\text{trans}}} + \frac{\rho D_{\text{int}}}{\eta} C_{\text{int}} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right)^2 \sum \frac{C_k}{Z_k} \right], \quad (2)$$

where λ is thermal conductivity, η is viscosity, M is molecular weight, ρ is density, D_{int} is the average coefficient for the diffusion of internal energy, $C_{v_{\text{trans}}}$ and C_{int} are the translational and the internal contributions to the molar heat capacity, Z_k is the number of collisions for relaxation of the k^{th} internal mode, and C_k is the heat capacity associated with that mode. In small rigid polyatomic molecules, the only collision numbers small enough to affect thermal conductivity significantly are those associated with rotational relaxation. For nonpolar gases, D_{int} is commonly assumed to be equal to the self-diffusion coefficient, D_{11} . For polar gases, however, Mason and Monchick¹ suggest that

$$D_{\text{int}} = \frac{D_{11}}{(1 + \delta)}, \quad (3)$$

where δ is a correction term calculated from the theory of resonant collisions. Mason and Monchick¹ have developed expressions from which the resonant correction for linear dipoles and symmetric tops can be computed. The expression used in the analysis of the linear dipoles HCl and DCl is as follows:

$$\delta = \langle a_4 \rangle \left(\frac{3}{16} \frac{\mu h}{\sigma_D kT} \right)^2 \left[\frac{m^{1/2}}{(C_{\text{int}}/R) I^{3/2}} \right]. \quad (4)$$

Here $\langle a_4 \rangle$, taken to be 0.44, is the mean value of a dimensionless quantity involving the rotational quantum numbers, μ is the dipole moment, h is Planck's constant, σ_D is the kinetic-theory diameter characteristic of diffusion ($\sigma_D \equiv \sigma[\Omega^{(1,1)*}]^{1/2}$ in the notation of Ref. 10), k is the Boltzmann constant,

m is the molecular mass, R is the universal gas constant, and I is the molecular moment of inertia. For near-spherical top dipoles such as NH_3 and ND_3 , the expression for δ is somewhat more complicated than Eq. (4), as a result of the presence of three moments of inertia, two of which are equal. This relation is

$$\delta = \frac{5\pi}{16} \langle a_4 \rangle \left(\frac{3}{16} \frac{\mu h}{\sigma_D kT} \right)^2 \frac{R}{C_{\text{int}}} \frac{m^{1/2}}{I_A(I_B)^{1/2}} \left(\frac{5}{4} - \frac{I_B}{4I_A} \right)^{-7/2}, \quad (5)$$

where I_A is the moment of inertia about the dipole axis and $I_B = I_C$ are the other two moments. For spherical top molecules such as CH_4 and CD_4 , the three moments of inertia are equal. It is easily seen that when $I_A = I_B = I_C$, Eq. (5) differs from Eq. (4) only by the factor $5\pi/16$.

The method of analysis of the pure gas data is quite different from the procedure used with the equimolar mixtures. Thus, it seems desirable to discuss all the pure gas results first and then follow this with all the mixture results, rather than to discuss both pure gas and mixture results for each gas pair before proceeding to the next system.

Pure Gases

The experimental data on all the pure gases were analyzed as follows: The necessary resonant corrections were calculated from Eqs. (4) and (5) and the results were used to compute D_{int} from Eq. (3). The collision number Z_{rot} was then calculated from Eq. (2) after λ had been replaced by the experimentally determined thermal conductivity. The ratio of the collision number of the deuterated gas to that of its undeuterated counterpart was then compared with a theoretical value based on the results of Sather and Dahler^{11,12} for a rough sphere:

$$Z_{\text{rot}}^{-1} \propto \frac{\left(\frac{4I/m\sigma^2}{\eta} \right)}{\left(1 + \frac{4I/m\sigma^2}{\eta} \right)^2}. \quad (6)$$

Here m and I are the same as in Eq. (4), while σ_η is the viscosity collision diameter ($\sigma_\eta \equiv \sigma[\Omega(2,2)^*]^{1/2}$ in the notation of Ref. 10) and σ is the diameter of the rough sphere core. The rough sphere model was chosen because the experimental results of O'Neal and Brokaw for a variety of near-spherical molecules (including methane and even ethane) suggest that this model is a reasonable one for substances that do not differ markedly from spherical symmetry.

Some temperature-independent properties necessary for the data analysis are listed in Table IV. Certain temperature-dependent quantities that are also needed for the data analysis are shown separately for each gas pair in Tables V to VII. The viscosity values for ammonia were taken from the best curve through the most recent viscosity data available.¹³⁻¹⁶ Viscosities of ND_3 and N^{15}H_3 were calculated from the NH_3 viscosities. Since there were no data available that compared the viscosities of the isotopic pairs, the viscosity collision cross sections for all three gases were assumed to be the same. Similarly, the viscosities for HCl listed in Table VI were taken from the best curve through the data available in the literature,¹⁷⁻²⁰ and the viscosity for DCl computed from these data, again with the assumption that the viscosity collision cross sections are equal. The viscosities for CH_4 were obtained by interpolation from the data of De Rocco and Halford.²¹ Viscosities of CD_4 were computed assuming the viscosity collision cross section of CH_4 is 2.2 percent larger than that of CD_4 . This was deduced from the viscosity measurements of van Isterbeek²² and suggests that the polarizability of CH_4 is somewhat larger than that of CD_4 . A similar effect has been observed and discussed for the $\text{H}_2 - \text{D}_2$ system.²³

The heat capacity data given in Tables V to VII were calculated from spectroscopic constants²⁴ by a computer program described by McBride, et al.²⁵ The heat capacity values for N^{15}H_3 at 300.0° and 424.2° K were obtained from the calculated

NH_3 and ND_3 heat capacities by interpolation on the basis of the square root of the reduced mass. As one would expect, the heat capacities for N^{15}H_3 are only slightly different from those for NH_3 ; the N^{15}H_3 heat capacity is larger by just over one part per thousand.

The dimensionless quantity $\rho D_{11}/\eta$ that involves the self-diffusion coefficient was computed as $(6/5)\langle A^* \rangle$.¹⁰ The quantity $\langle A^* \rangle$ is a ratio of collision integrals (essentially the ratio of the viscosity and diffusion cross sections) and is quite insensitive to temperature and the details of the intermolecular force law, at least for spherically symmetric potentials. Since there is no experimental information on the self-diffusion of ammonia and only room temperature data for hydrogen chloride, $\langle A^* \rangle$ was taken from calculations for a modified (angle independent) Stockmayer potential.²⁶ The values of $\langle A^* \rangle$ used for methane were taken from calculations based on an exponential-6 potential²⁷ ($\alpha = 14$, $\epsilon/k = 152.8$). The determination of $\langle A^* \rangle$ is the only place in the analysis where it is necessary to make any assumption about the intermolecular force law.

All the expressions, molecular properties, temperature-dependent quantities, and procedures necessary for the data analysis have now been presented. The first gas pair that will be discussed is CH_4 - CD_4 . The analysis is the simplest for this system since these molecules are spherical tops with no dipole moments; therefore, the resonant correction is zero [see Eq. (5)]. Thus $\rho D_{\text{int}}/\eta$ is taken to be $\rho D_{11}/\eta$ and is computed as $(6/5)\langle A^* \rangle$ as before. By substituting the experimentally determined thermal conductivity into Eq. (2), the collision number Z_{rot} is easily calculated for both CH_4 and CD_4 .

Collision numbers for rotational relaxation calculated by this procedure, as well as the ratios of Z_{CD_4} to Z_{CH_4} , are presented in Table V. The ratio obtained by substituting the appropriate quantities from Table IV into Eq. (6)

is $Z_{\text{CD}_4}/Z_{\text{CH}_4} = 0.6502$.

The room temperature collision number for methane is considerably lower than the value of 9 collisions obtained by the temperature recovery factor method,¹² which also utilizes Eq. (2). The value of Z_{rot} decreases with increasing temperature as did the Z_{rot} for H_2O .² It is interesting to note that collision numbers for SO_2 , recently calculated from experimental thermal-conductivity data²⁸ by means of Eq. (2), increase with increasing temperature. However, too much significance should not be placed on these temperature trends since the collision number is extremely sensitive to the absolute value of the thermal conductivity.

The agreement between the ratios of the experimentally determined collision numbers and the theoretical ratio obtained from Eq. (6) is quite good at the higher temperatures, whereas the experimental ratios are somewhat higher than the theoretical value at the lower temperatures. It should be emphasized that the ratio of Z numbers is extremely sensitive to the ratio of the viscosity cross sections. For example, if one assumes that these cross sections are equal (rather than $\sigma_{\text{CH}_4}^2/\sigma_{\text{CD}_4}^2 = 1.022$ as deduced from viscosity data²²) the ratio of Z numbers becomes about unity.

In summary, for nonpolar spherical tops, rotational collision numbers obtained from experimental thermal conductivity data by means of Eq. (2) are in reasonable agreement with current theory for rough spheres, a conclusion previously reached by O'Neal and Brokaw.¹²

As far as polar molecules are concerned, the analysis is simplest for linear dipoles such as HCl and DCl . Rotational relaxation collision numbers obtained from the experimental conductivities and resonant corrections calculated from Eq. (4) are given in Table VI. The room temperature value for Z_{rot} is in good agreement with the $Z_{\text{rot}} \sim 7$ collisions, recently obtained by Breazeale and

Kneser²⁹ at 0° C, using the acoustic absorption technique. On the other hand, if collision numbers are calculated with the assumption that the resonant correction is zero, values are obtained (1.2 - 1.3 collisions) that are abnormally low when compared with this experimental value. That a collision number of even 6 or 7 for HCl is surprisingly low can readily be seen by comparing it with the Z_{rot} for N_2 . The moment of inertia of N_2 is a little more than five times greater than the moment of inertia for HCl, whereas their masses are about the same. Thus, on the basis of Eq. (6), one would expect Z_{rotHCl} to be about four times greater than Z_{rotN_2} , which is about 5.5 collisions.³⁰ Breazeale and Kneser have attributed the low Z_{rot} for HCl to its large dipole moment, and it is probable that the enhanced efficiency with which HCl molecules relax rotational energy is due to the long-range dipole-dipole interaction. The collision numbers for DCl are nearly independent of temperature; however, those for HCl clearly decrease with increasing temperature. The agreement between the ratios of the collision numbers obtained from experiment and the theoretical ratio is satisfactory. (In contrast, the ratios of the collision numbers calculated with the assumption that the resonant correction is zero are all unity, clearly in disagreement with all current theories on rotational relaxation.)

The final system of pure polar gases to be analyzed includes NH_3 , ND_3 , and N^{15}H_3 . Rotational relaxation collision numbers calculated from the experimental data and resonant corrections calculated from Eq. (5)³¹ are given in Table VII. The $Z_{\text{rot}} = 2.3$ collisions obtained for NH_3 at 300° K is much smaller than the value of 9 collisions quoted by Herzfeld and Litovitz,³² but it is in agreement (as it should be) with the value of 1.8 collisions obtained by Mason and Monchick¹ by fitting thermal conductivity data. In addition, the NH_3 value of 2.3 collisions is consistent with the 4.0 collisions obtained for CH_4 (see Table V); their masses

and moments of inertia are similar but NH_3 has a large dipole moment (which makes for a small Z_{rot}), while methane is nonpolar. Again, Z_{rot} shows a decrease with increasing temperature, the dependence being much the same as that obtained for H_2O .² The agreement between the ratios of the experimentally derived collision numbers and the theoretical ratio is comparable to that obtained for the other two systems. Unlike the previous results, however, the agreement is better at the lower temperatures than at the higher ones.

In summary, the data on the pure gases seem to support the conclusion reached on the basis of the pure H_2O and D_2O results; that is, all in all, the data appear to agree with the formula of Mason and Monchick for the thermal conductivity of polyatomic gases [Eq. (2)] and with the correction to this expression necessary for highly polar gases [Eq. (3)].

Equimolar Mixtures

In a recent paper² on H_2O - D_2O , we pointed out that Mason and Monchick's postulate regarding resonant exchange of rotational energy could be qualitatively tested by comparing the thermal conductivity of two polar gas pairs with that of their equimolar mixture. The resonant effect is based on a matching of rotational energy levels. Consider, for example, an equimolar mixture of HCl and DCl . In such a mixture, one-half the collisions are self-collisions of HCl and DCl in which resonant exchange of rotational quanta may occur. The remaining collisions are between HCl and DCl . Since the differences between rotational energy levels in DCl are about half as large as the differences in HCl , exchange is not possible, at least for certain collisions. Consequently, such a mixture might be expected to have a thermal conductivity somewhat greater than either of the pure constituents.

The thermal conductivities of the equimolar CH_4 - CD_4 mixtures illustrate the results that would be expected if no resonant effect were involved because CH_4

and CD_4 are nonpolar. These results are presented in Table VIII along with thermal conductivities of the mixtures calculated assuming a linear mixing rule. (The equations of Monchick, Pereira, and Mason⁵ were used for a sample calculation at 300° K and agreed with this linear average to within one part in ten thousand.) The experimental conductivities agree with the calculated values to within 2-3 parts per thousand. The experimental values are higher than the calculated values at all temperatures; this suggests that the very slight positive deviation from a linear mixing rule may be caused by a slightly smaller cross section for the unlike interaction.

The next system for analysis and discussion is the equimolar HCl-DCI mixture. The experimental conductivities will be compared with values calculated using the first-order linearized form of the equations of Monchick, Pereira, and Mason⁵ mentioned in the introduction. This form of their results can be regarded as equivalent to the Hirschfelder-Eucken formula for the thermal conductivity of polyatomic gas mixtures³³ plus a large number of first-order correction terms.

In calculating the mixture conductivity it is necessary to know the value of the resonant correction for the various interactions in order to compute the coefficient of diffusion for internal energy [see Eq. (3)]. For the like interactions, these corrections will be the same as for the pure gases; for the unlike interactions the situation is more complicated. If the resonance effect actually requires an exact matching of rotational energy differences, the correction for the unlike interactions would be zero. There is recent evidence, however, that rotational energy exchange does take place in HCl-DCI collisions.³⁴ That such an exchange is reasonable can be shown by the following arguments. The rotational energy of a diatomic molecule is given by

$$\epsilon_{\text{rot}} = J(J + 1)\theta_{\text{rot}}/T, \quad (7)$$

where $\theta_{\text{rot}} = h^2/8\pi^2 k I_{\text{rot}}$ and J is the rotational quantum number. Since rotational transitions are generally restricted to those for which $\Delta J = \pm 1$, the energy difference between rotational levels J and $J + 1$ is

$$\epsilon_{J+1} - \epsilon_J = \left(\frac{\theta_{\text{rot}}}{T} \right) 2J. \quad (8)$$

The ratio of the moment of inertia of DCl to that of HCl is 1.9448 (see Table IV); therefore, $\theta_{\text{rot}_{\text{DCl}}} = \theta_{\text{rot}_{\text{HCl}}}/1.9448$. Thus, the rotational energy level differences for HCl and DCl in units of $\theta_{\text{rot}_{\text{HCl}}}/T$ are as follows:

HCl		2		4		6	
		(J = 1)		(J = 2)		(J = 3)	etc.
DCl	1.028	2.057	3.085	4.114	5.142	6.170	
	(J = 1)	(J = 2)	(J = 3)	(J = 4)	(J = 5)	(J = 6)	etc.

It is evident that, as a consequence of the moment of inertia of DCl being nearly twice that of HCl, near-resonant collisions are always possible for an HCl molecule interacting with a DCl molecule, whereas for DCl interacting with HCl, near-resonant collisions are possible for only half the energy levels. On this basis, the following values for the resonant correction were assumed:

$$\delta_{\text{HCl-DCl}} = \delta_{\text{HCl-HCl}}, \quad (9a)$$

and

$$\delta_{\text{DCl-HCl}} = \frac{\delta_{\text{DCl-DCl}}}{2}. \quad (9b)$$

The results of the mixture calculations are presented in Table IX and are shown graphically in Fig. 2. The method referred to as "inelastic" uses the equations of Monchick, Pereira, and Mason.⁵ The Hirschfelder-Eucken calculations, which involve no inelastic effects, are also given in order to show the magnitude of the first-order correction terms. In addition, both these calculations were carried out with the assumption that there was no resonant exchange during unlike

collisions ($\delta_{\text{HCl-DCl}} = \delta_{\text{DCl-HCl}} = 0$), which would be the case if the rotational exchange process actually required an exact resonance. The experimentally determined conductivities are also listed in Table IX. The experimental points plotted in Fig. 2 have an apparent smoothness of about five parts in ten thousand.

It is quite clear that the conductivities obtained when no unlike interaction is assumed are much too large; however, both methods give very satisfactory agreement with experiment when unlike interaction is taken into account. In fact, the conductivities obtained from the inelastic calculations agree with experiment to within one part per thousand. Monchick, Pereira, and Mason⁵ concluded that for most purposes the Hirschfelder-Eucken mixture formula is satisfactory for nonpolar gases or a mixture of a nonpolar and a polar gas provided that inelastic effects are included in calculations for the pure components. It appears that their conclusion also holds for a mixture of polar gases, at least for an equimolar HCl-DCl mixture.³⁵

The final system to be discussed is that of ammonia and its isotopically substituted counterparts. The thermal conductivity of equimolar NH_3 - ND_3 was measured at 300° K (see Table III). The mixture conductivity was surprisingly low; indeed, the conductivities of both pure NH_3 and pure ND_3 are greater than that of the mixture. NH_3 and ND_3 exchange rapidly in a glass vessel even at room temperature,³⁶ which results in a four-component system: NH_3 , ND_3 , NH_2D , and NHD_2 . Part of the discrepancy in the mixture conductivity can be rationalized on the basis of the lower heat capacities of NH_2D and NHD_2 .

Because of the complexity of the NH_3 - ND_3 mixture, we decided to test the exact resonance requirement using the equimolar NH_3 - N^{15}H_3 mixture instead. For this mixture, the composition will remain constant despite any exchange reactions

that might take place. From Table III, it is apparent that the mixture conductivity lies midway between that of the pure components. In fact, the weighted average of the conductivities of the two components agrees with the mixture conductivity to less than one part per thousand. In the light of the HCl-DCI results, it seems quite clear that despite the lack of exact rotational energy level differences (the moments of inertia differ by about 0.3 percent) rotational exchange is occurring. Otherwise, the conductivity of the mixture would be considerably larger (about 4 percent) than the average of the pure components.

CONCLUDING REMARKS

The experimental results are consistent with the notion that a resonant, or near-resonant exchange of rotational quanta is important in determining the thermal conductivity of polar gases. This is substantiated by measurements on the pure compounds and also on HCl-DCI and $N^{14}H_3-N^{15}H_3$ mixtures.

Results on NH_3-ND_3 and also H_2O-D_2O mixtures² are complicated since exchange reactions occur,⁴ and these are in fact multicomponent systems. Nonetheless, it seems likely that these data can also be explained in terms of considerable near-resonant exchange between unlike molecules and somewhat larger collision cross sections for unsymmetric species such as NH_2D , NHD_2 , and HDO .

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of summations by integrations. In the case of ammonia, Mason and Monchick¹
carried out the direct summation on a high-speed computer and found that the
analytic expression for the resonant correction gave values that were 5 per-
cent too large at 273° K and 0.9 percent too large at 573° K. Thus the ratio
of δ [Eq. (5)] to δ [direct summation] as a function of temperature can be
determined from a plot of δ [Eq. (5)]/ δ [summation] against $h^2/(8\pi^2 k I_A) T$.
This procedure was applied in computing the δ values (shown in Table VII)
used in determining Z_{rot} from conductivity data.

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35. It should be mentioned that the HCl-DCl system is actually a four-component system due to the existence of two chlorine isotopes, Cl^{35} and Cl^{37} . However, the moments of inertia of HCl^{35} and HCl^{37} , as well as DCl^{35} and DCl^{37} , differ by only 2-3 parts per thousand. Since rotational exchange appears to be possible between HCl-DCl, there is no doubt that it would occur between HCl^{35} - HCl^{37} , etc.
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Table I. - Experimental electromotive force (emf)
measurements relative to argon (mV).

Gas	Temperature, °K				
	299.8	333.0	375.5	423.3	472.3
He	52.253	49.342	46.068	42.822	40.364
N ₂	17.700	16.671	15.552	14.359	13.583
CH ₄	28.009	27.657	27.392	27.003	26.692
CD ₄	28.878	28.941	28.911	28.550	28.154
0.52 CH ₄ -0.48 CD ₄	28.483	28.353	28.215	27.840	27.491
Gas	Temperature, °K				
	300.0	329.1	374.6	424.2	474.5
He	55.796	53.174	46.331	43.097	40.313
N ₂	18.872	17.968	15.611	14.509	13.523
NH ₃	18.437	19.548	19.607	20.584	21.173
ND ₃	18.286	19.755	20.119	21.276	21.938
0.5 NH ₃ -0.5 ND ₃	17.857	-----	-----	-----	-----
N ¹⁵ H ₃	17.398	-----	-----	19.921	-----
0.52 NH ₃ -0.48 N ¹⁵ H ₃	17.963	-----	-----	20.295	-----
Gas	Temperature, °K				
	300.1	328.5	374.8	423.1	471.4
He	52.375	49.615	46.040	43.076	40.504
N ₂	17.736	16.765	15.509	14.476	13.563
HCl	-12.647	-11.010	-8.574	-6.304	-4.394
DCl	-12.968	-11.162	-8.564	-6.066	-3.963
0.5 HCl-0.5 DCl	-12.473	-10.749	-8.339	-6.008	-4.066

Table II. - Thermal conductivities
of helium and argon assumed
for calibration purposes
($\mu\text{cal cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{K}^{-1}$).

Temperature, $^{\circ}\text{K}$	Helium	Argon
299.8	370.7	42.39
300.0	370.9	42.42
300.1	371.0	42.43
328.5	394.5	45.50
329.1	395.0	45.55
333.0	398.2	45.99
374.6	432.0	50.50
374.8	432.2	50.53
375.5	432.8	50.60
423.1	471.4	55.52
423.3	471.6	55.54
424.2	472.3	55.62
471.4	508.9	60.15
472.3	509.5	60.23
474.5	511.2	60.44

Table III. - Experimental thermal conductivities
($\mu\text{cal cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{K}^{-1}$).

Gas	Temperature, $^{\circ}\text{K}$				
	299.8	333.0	375.5	423.3	472.3
CH_4	80.70	91.21	106.55	125.17	144.48
CD_4	83.03	95.57	113.51	134.86	156.47
0.52 CH_4 -0.48 CD_4	81.96	93.52	110.21	130.23	150.80
N_2	60.56 ₀	65.59	72.10	78.87	85.65
Gas	Temperature, $^{\circ}\text{K}$				
	300.0	329.1	374.6	424.2	474.5
NH_3	59.96	67.51	80.64	96.13	112.58
ND_3	59.76	67.86	81.91	98.54	116.20
0.5 NH_3 -0.5 ND_3	59.19	-----	-----	-----	-----
N^{15}H_3	58.60	-----	-----	93.93	-----
0.52 NH_3 -0.48 N^{15}H_3	59.33	-----	-----	95.16	-----
N_2	60.55 ₅	64.98	71.89	79.12	85.83
Gas	Temperature, $^{\circ}\text{K}$				
	300.1	328.5	374.8	423.1	471.4
HCl	34.95	38.03	43.39	49.17	54.90
DCl	34.80	37.95	43.40	49.38	55.37
0.5 HCl -0.5 DCl	35.04	38.18	43.56	49.34	55.26
N_2	60.60 ₂	64.90	71.92	78.91	85.35

Table IV. - Molecular properties of test gases.

Gas	Moments of inertia, $\text{g-cm}^2 \times 10^{40}$		Molecular weight	Dipole moment, $\text{esu-cm} \times 10^{18}$
	I_A	$I_B = I_C$		
CH_4	^a 5.3326	$= I_A$	16.0425	0
CD_4	^b 10.7073	$= I_A$	20.0678	0
NH_3	^c 4.4140	2.8087	17.0320	^d 1.477
N^{15}H_3	^c 4.4140	2.8159	18.0330	^e 1.477 ₂
ND_3	^c 8.7960	5.4129	20.0500	^d 1.509
HCl	-----	^{f, g} 2.6431	^g 36.4693	^h 1.081
DC1	-----	^{f, i} 5.1404	^g 37.4763	^h 1.085

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^eInterpolated from data for NH_3 and ND_3 on basis of the reduced mass.

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^gWeighted average of the molecular properties of HCl³⁵ and HCl³⁷.

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ⁱWeighted average of the molecular properties of DC1³⁵ and DC1³⁷.

Table V. - Data analysis for pure CH₄ and CD₄.

	Temperature, °K				
	299.8	333.0	375.5	423.3	472.3
Viscosity of CH ₄ , μP	112.5	123.3	136.0	150.0	163.6
(C _{int} /R) CH ₄	1.80134	1.96780	2.22166	2.54276	2.89179
CD ₄	2.39526	2.70998	3.12661	3.59446	4.06090
$\rho D_{11}/\eta (=6/5\langle A^* \rangle)$	1.3190	1.3187	1.3184	1.3194	1.3207
Z _{rot} CH ₄	4.0	3.6	3.8	3.6	3.0
CD ₄	3.4	2.8	2.7	2.4	2.0
$\frac{Z_{rot, (CD_4)}}{Z_{rot, (CH_4)}}$	0.86	0.79	0.71	0.67	0.66
$\left[\frac{Z_{rot, (CD_4)}}{Z_{rot, (CH_4)}} \right]_{Calc, Eq. (6)}$	0.65	0.65	0.65	0.65	0.65

Table VI. - Data analysis for pure HCl and DCl.

		Temperature, °K				
		300.1	328.5	374.8	423.1	471.4
Viscosity of HCl, μP		146.4	160.7	183.8	207.3	229.0
(C_{int}/R)	HCl	1.00430	1.00501	1.00704	1.01116	1.01834
	DCl	1.00859	1.01346	1.02658	1.04799	1.07709
$\rho D_{11}/\eta (=6/5\langle A^* \rangle)$		1.3254	1.3243	1.3232	1.3214	1.3190
Z_{rot}	HCl	6.2	4.6	3.6	3.2	3.0
	DCl	2.6	2.3	2.0	1.9	1.9
$\frac{Z_{\text{rot, (DCl)}}}{Z_{\text{rot, (HCl)}}$		0.43	0.50	0.56	0.60	0.62
$\left[\frac{Z_{\text{rot, (DCl)}}}{Z_{\text{rot, (HCl)}}} \right]_{\text{Calc, Eq. (6)}}$		0.54	0.54	0.54	0.54	0.54
δ	HCl	0.48	0.42	0.34	0.28	0.24
	DCl	0.18	0.16	0.13	0.10	0.09

Table VII. - Data analysis for pure NH_3 , N^{15}H_3 and ND_3 .

		Temperature, °K				
		300.0	329.1	374.6	424.2	474.5
Viscosity of NH_3 , μP		101.53	112.2	129.0	147.2	165.8
(C_{int}/R)	NH_3	1.78007	1.87133	2.02926	2.21460	2.40886
	ND_3	2.10154	2.25252	2.49342	2.75482	3.01423
	N^{15}H_3	1.778205	-----	-----	2.21792	-----
$\rho D_{11}/\eta (=6/5\langle A^* \rangle)$		1.3202	1.3218	1.3241	1.3254	1.3243
Z_{rot}	NH_3	2.3	2.1	1.9	1.7	1.6
	ND_3	1.6	1.5	1.3	1.3	1.2
	N^{15}H_3	2.5	---	---	1.8	---
$\frac{Z_{\text{rot}, (\text{ND}_3)}}{Z_{\text{rot}, (\text{NH}_3)}}$		0.69	0.70	0.72	0.74	0.77
$\left[\frac{Z_{\text{rot}, (\text{ND}_3)}}{Z_{\text{rot}, (\text{NH}_3)}} \right]_{\text{Calc, Eq. (6)}}$		0.64	0.64	0.64	0.64	0.64
δ	NH_3	0.15	0.12	0.09	0.07	0.06
	ND_3	0.05	0.04	0.03	0.02	0.02
	N^{15}H_3	0.15	----	----	0.07	----

Table VIII. - Comparison of the experimental $\text{CH}_4\text{-CD}_4$ mixture thermal conductivities with those calculated using the linear mixing rule ($\mu\text{cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{K}^{-1}$).

	Temperature, $^\circ\text{K}$				
	299.8	333.0	375.5	423.3	472.3
0.52 CH_4 -0.48 CD_4 , (exptl)	81.96	93.52	110.21	130.23	150.80
0.52 CH_4 -0.48 CD_4 , (calc, mixing rule)	^a 81.82	93.32	109.91	129.85	150.27
$\lambda, (\text{exptl}) / \lambda, (\text{calc})$	1.0017	1.0022	1.0027	1.0029	1.0035

^aThe pure gas conductivities are given in Table III.

Table IX. - Comparison of experimental and calculated values for thermal conductivity of equimolar HCl-DCI mixtures ($\mu\text{cal cm}^{-1} \text{sec}^{-1} \text{ }^{\circ}\text{K}^{-1}$).

Method	Temperature, $^{\circ}\text{K}$				
	300.1	328.5	374.8	423.1	471.4
Inelastic, unlike interaction	35.08	38.21	43.62	49.49	55.33
Inelastic, no unlike interaction	36.35	39.59	45.09	50.99	56.80
Hirschfelder-Eucken, unlike interaction	34.98	38.09	43.48	49.36	55.22
Hirschfelder-Eucken, no unlike interaction	35.58	38.64	44.01	49.88	55.75
Linear mixing rule $\left(\frac{\lambda_{\text{exptl HCl}} + \lambda_{\text{exptl DCl}}}{2} \right)$	34.87	37.99	43.39	49.28	55.13
Experimental	35.04	38.18	43.56	49.43	55.26

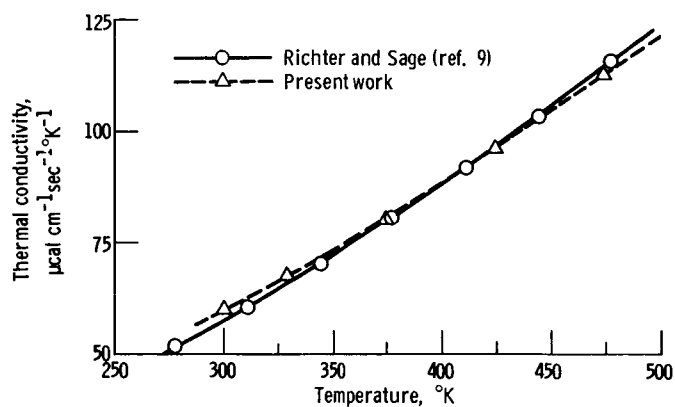


Fig. 1. - Comparison of ammonia data with recent literature values.

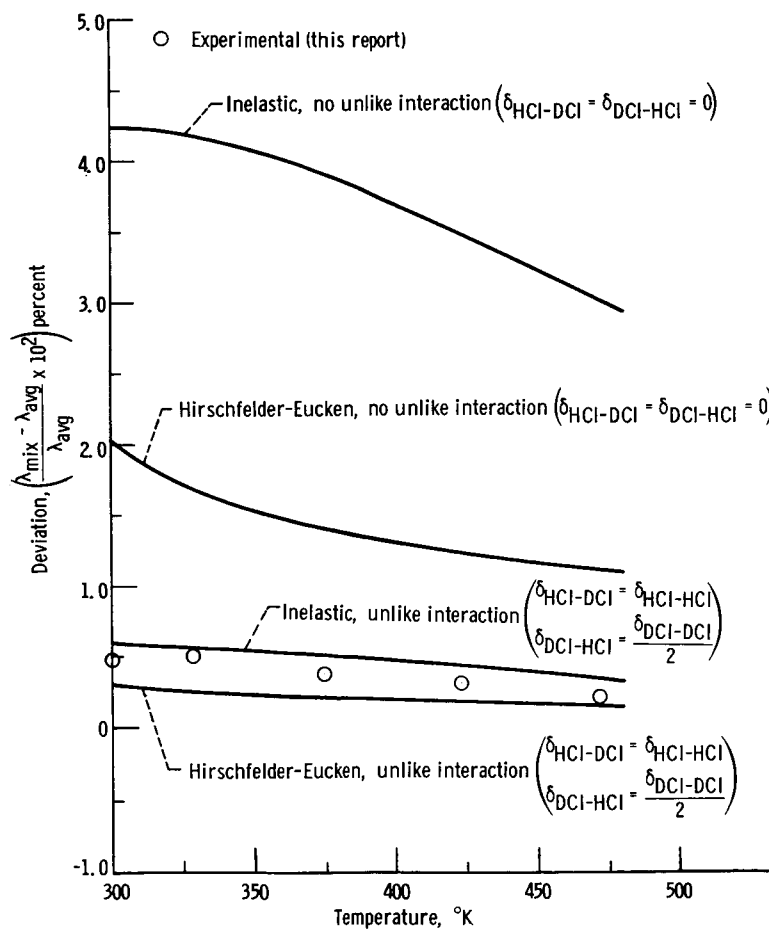


Fig. 2. - Deviation of the thermal conductivities of equimolar HCl-DCI mixtures from linear average.